Accurate band gaps of solids via efficient vertex corrections in *GW*

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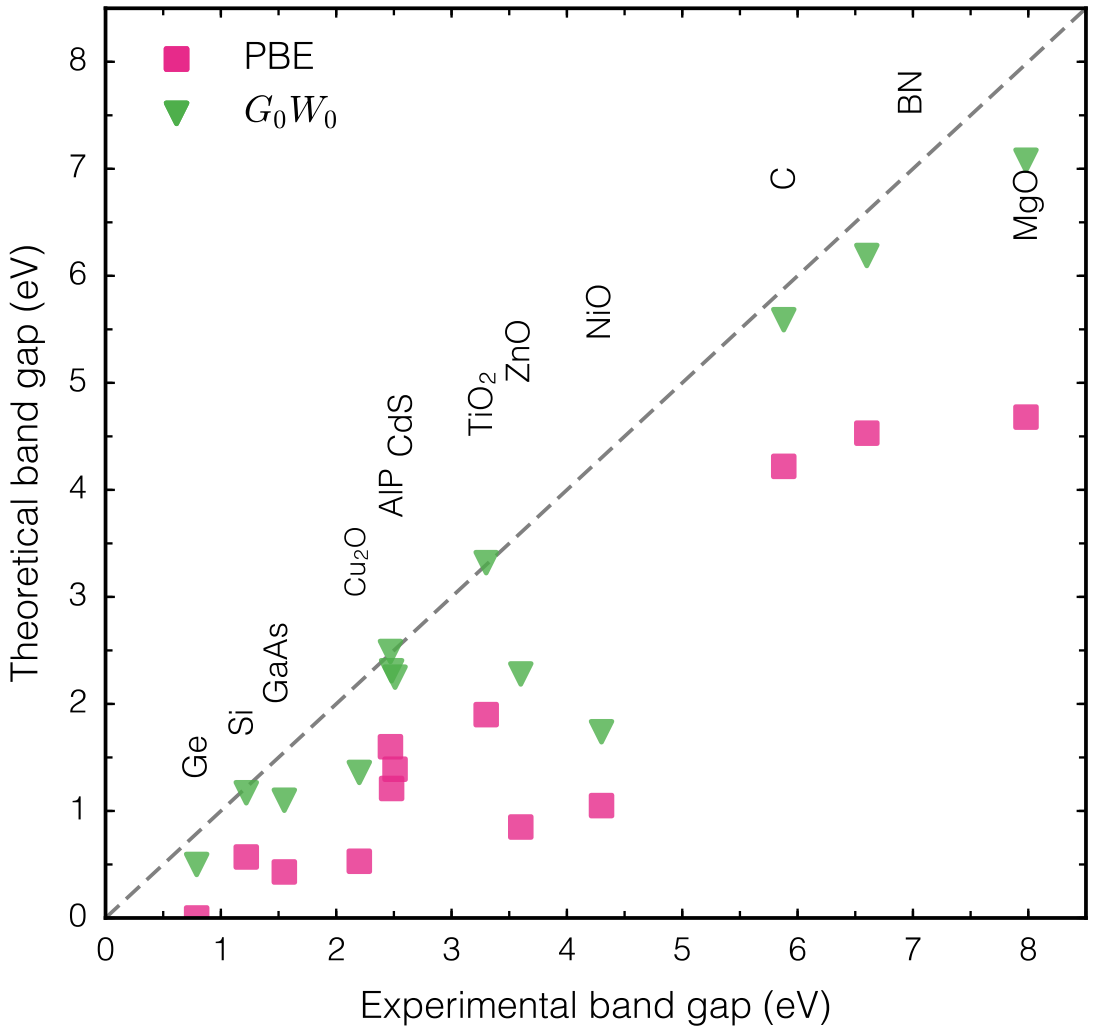
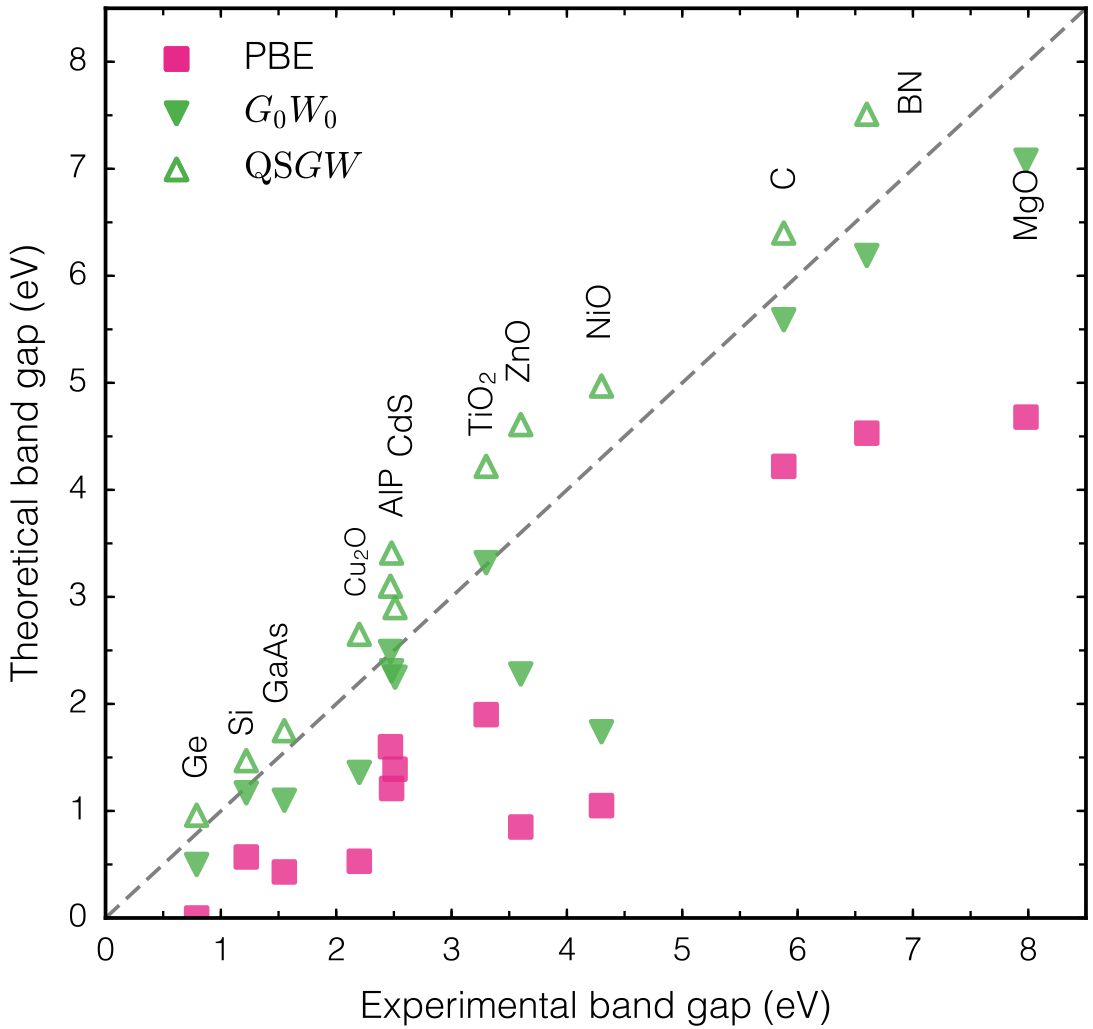
Band-gap problem with GW



- G_0W_0@PBE → underestimated E_g.

Band-gap problem with GW



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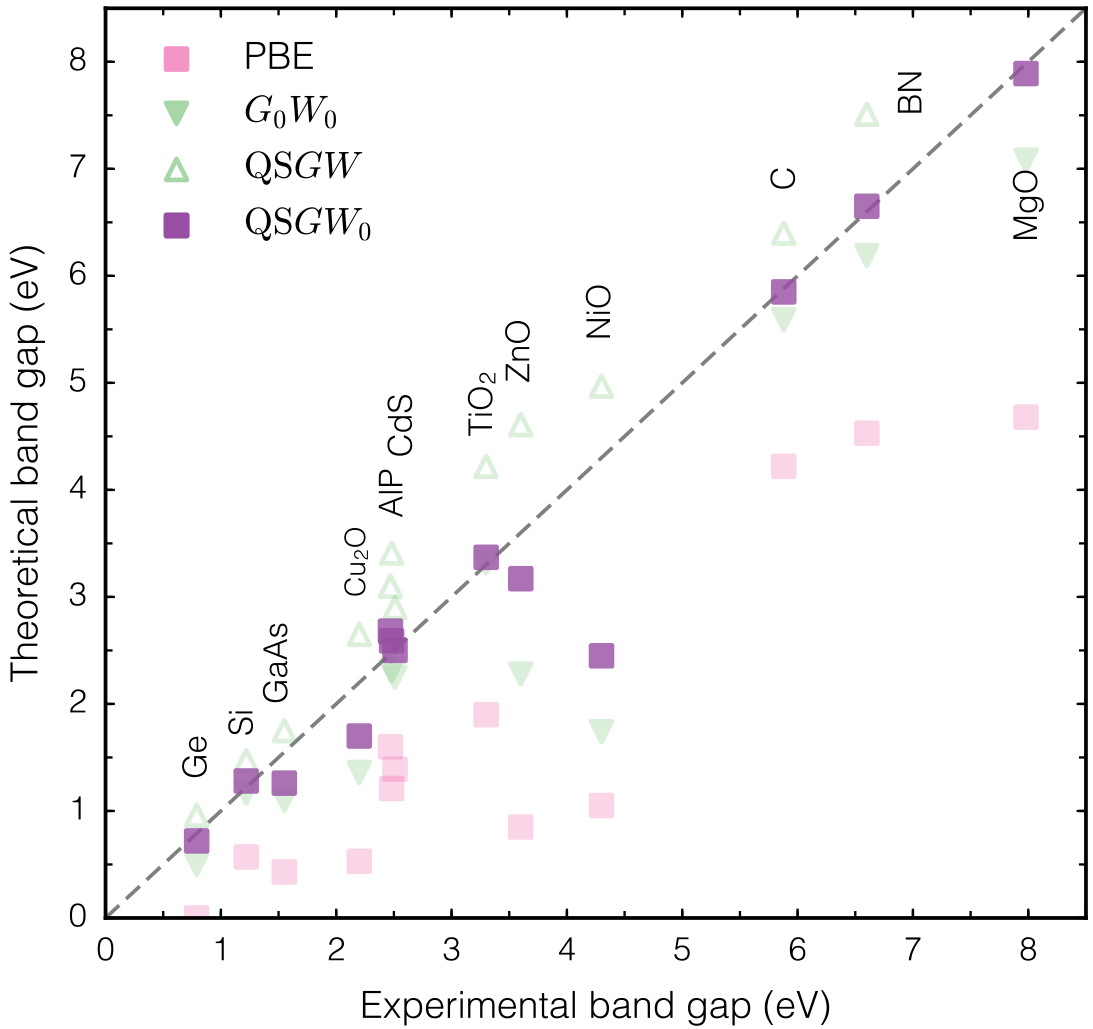

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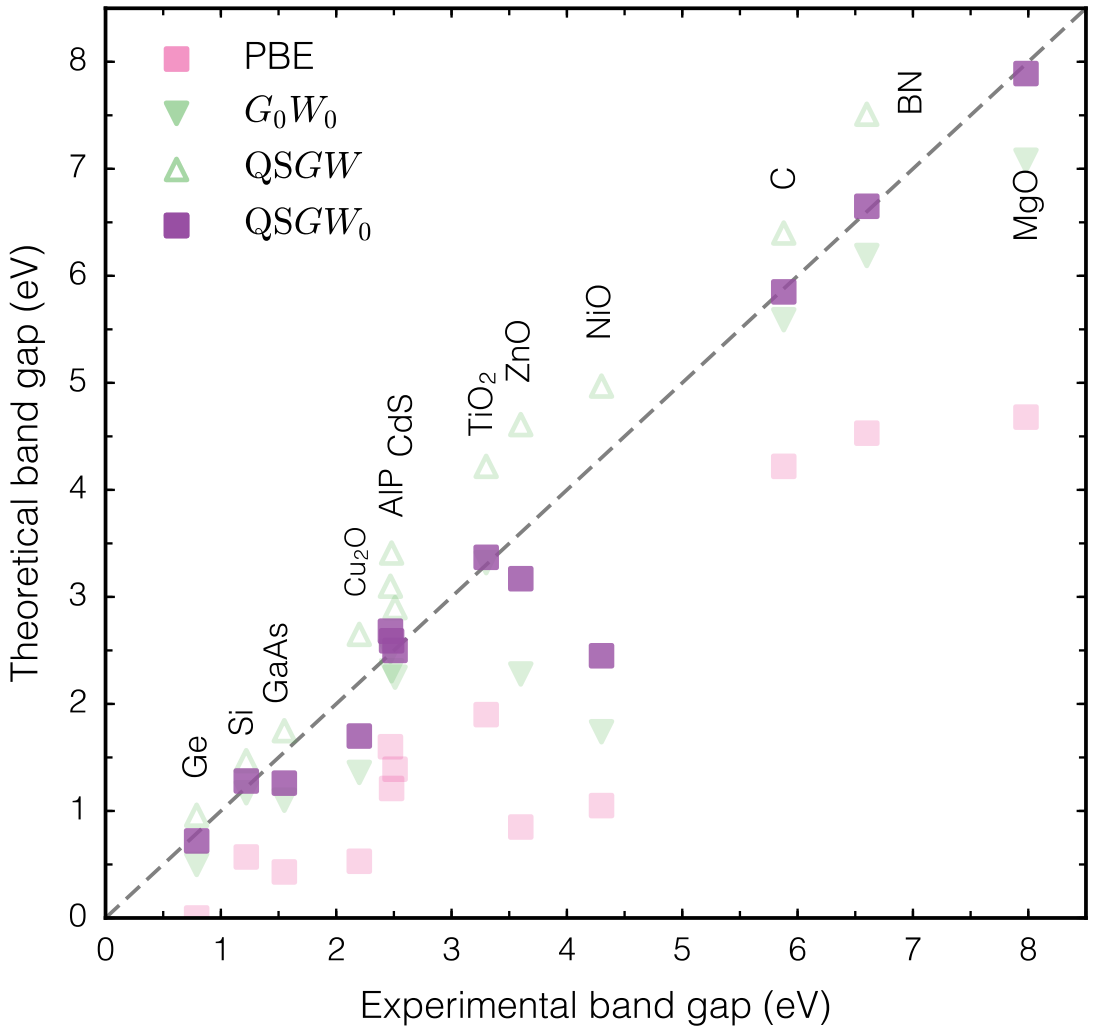
- QSGW_0@PBE → good E_g, but *not* always.

Band-gap problem with GW



- G_0W_0@PBE → underestimated E_g.
- Quasiparticle self-consistent QSGW → too large E_g, underscreened W.
- QSGW_0@PBE → good E_g, but *not* always.
- Vertex corections have to be included in W to go beyond RPA

$$W = \varepsilon^{-1} v$$
$$\varepsilon^{-1} = 1 + v\chi$$
$$\chi = \chi^0 + \chi^0 (v + f_{xc})\chi$$

A survey of f_{xc}

- NANOQUANTA kernel [a]

$$f_{xc}(34) = P_0^{-1}(36)G(65)G(5'6)W(55')G(57)G(75')P_0^{-1}(74)$$

as accurate as Bethe-Salpeter equation; *but computationally formidable.*

- Long-range contribution (LRC) kernel[b]

$$f_{xc}^{\mathrm{LRC}} = -(a + b\omega^2)/q^2$$

surprisingly good for semiconductors; cheap; *but empirical*; *not sufficient for insulators.*

- Adiabatic local density approximation (ALDA) kernel

$$f_{xc}^{\mathrm{ALDA}} = \frac{\partial V_{xc}^{\mathrm{LDA}}}{\partial \rho}$$

ineffective for solids (missing long-range behavior).

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[a] See e.g., Reining et al. (2002), Sottile, Olevano, and Reining (2003), Adragna, Del Sole, and Marini (2003), Marini, Del Sole, and Rubio (2003), and Bruneval et al. (2005).

[b] Reining et al. 2002; Botti et al. 2005.

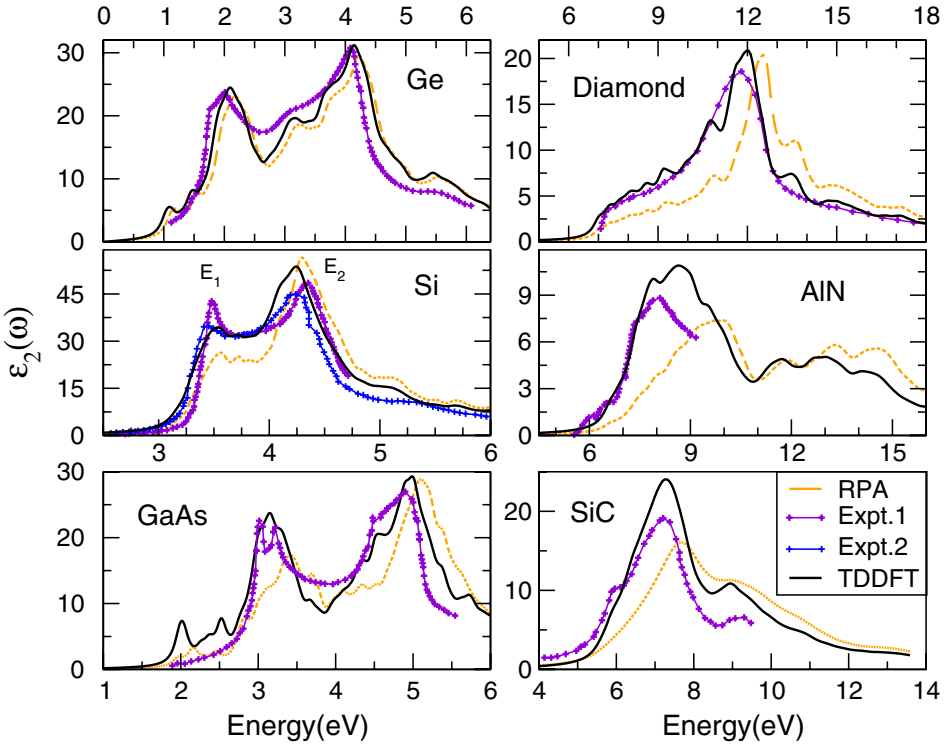
Bootstrap approximated f_{xc}

- (static) **BOOTSTRAP** kernel (Sharma, J. Dewhurst, et al. 2011)

$$f^{\text{boot}}_{xc,\mathbf{GG'}}(\mathbf{q},\omega) = \frac{\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},0)v_{\mathbf{G'}}(\mathbf{q})}{1-\varepsilon^{\text{RPA}}_{\mathbf{00}}(\mathbf{q},0)} = \frac{\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},0)v_{\mathbf{G'}}(\mathbf{q})}{\chi_{\mathbf{00}}(\mathbf{q},0)v_{\mathbf{G'}}(\mathbf{q})}$$

  - ✓ correct $1/q^2$ as $q \to 0$
  - ✓ small overhead to RPA
  - ✓ no empirical parameters

- It works well for absorption spectra of semiconductors.



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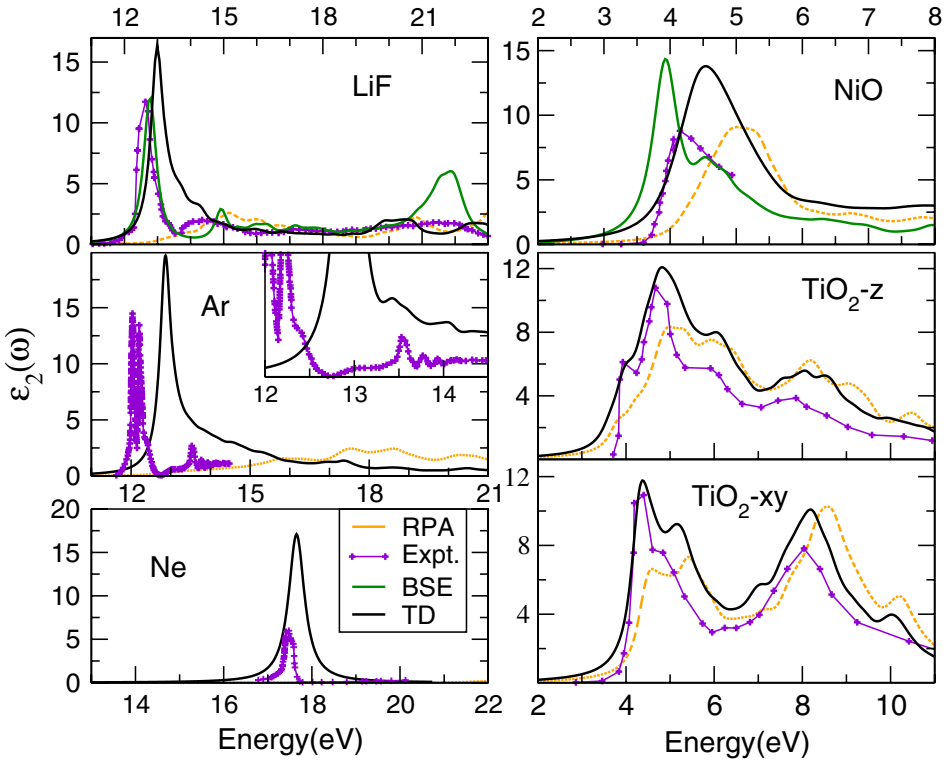
  - ✓ correct $1/q^2$ as $q \to 0$
  - ✓ small overhead to RPA
  - ✓ no empirical parameters

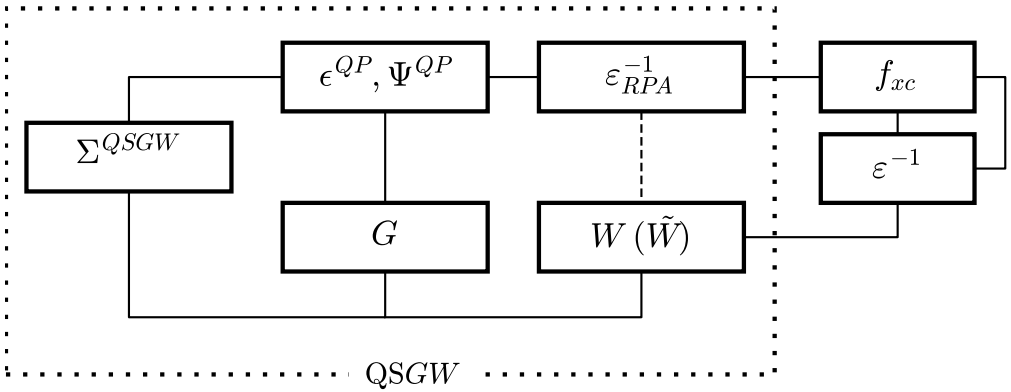
- It works well for absorption spectra of semiconductors.

- *Not* so well for wide-gap insulators (Rigamonti et al. 2015).



*Note that LiF and Ar were not converged here.

Implementation in ABINIT

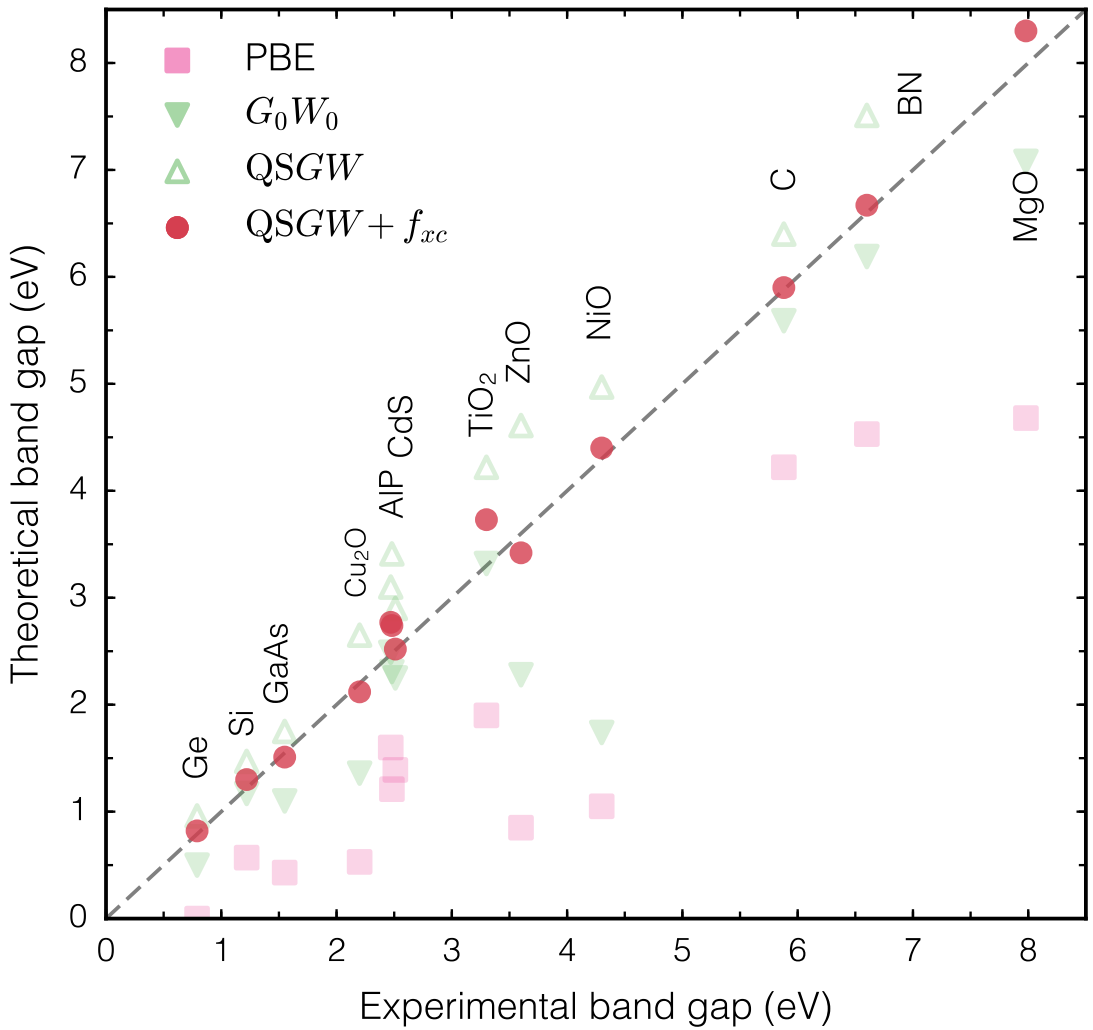



```
gwcalctyp 29
optdriver 3
gwgamma   -4
```

src/70_gw/m_screening.F90

```
chi00_head = chi0(1,1,1)*vc_sqrt(1)**2
nstep=50 ! iteration steps
do istep=1,nstep
  call atddft_symepsm1(io=1,...) !static
  converged = (conv_err <= tol4)
  if (converged) then
    call atddft_symepsm1(...)
  else if (istep < nstep) then
    chi0_tmp = chi0(:,:,1)
    vfxc_boot = chi0(:,:,1)/chi00_head
    vfxc_boot = vc_sqrt*vc_sqrt*vfxc_boot
  end if
end do
```

Accuracy



- Mean absolute error (eV)

QSGW+f_{xc}	**0.13**
QSGW	0.62
G_0W_0	0.45

- Highly accurate for a wide variety of materials:
  - ✓ sp semiconductor
  - ✓ wide-gap insulator
  - ✓ TM compound
  - ✓ correlated oxide

WC and AP, PRB **92**, 041115(R) (2015).

Accuracy

- BOOTSTRAP VS NANOQUANTA

	present[a]	NANOQUANTA[b]	Diff.
Si	−0.17	−0.17	0.00
SiC	−0.38	−0.35	0.03
C	−0.50	−0.39	0.11
AlP	−0.33	−0.33	0.00
Ge	−0.14	−0.14	0.00
GaAs	−0.25	−0.23	0.01
CdS	−0.67	−0.48	0.19
BN	−0.84	−0.55	0.29
MgO	−0.99	−1.04	0.06

Band-gap renormalization (eV) due to vertex corrections.

[a] Chen and Pasquarello 2015.

[b] Shishkin, Marsman, and Kresse 2007.

- BSE-like accuracy at a *marginal* computational cost.

Kernel variants

- RPA-BOOTSTRAP (Rigamonti et al. 2015, later Berger 2015)

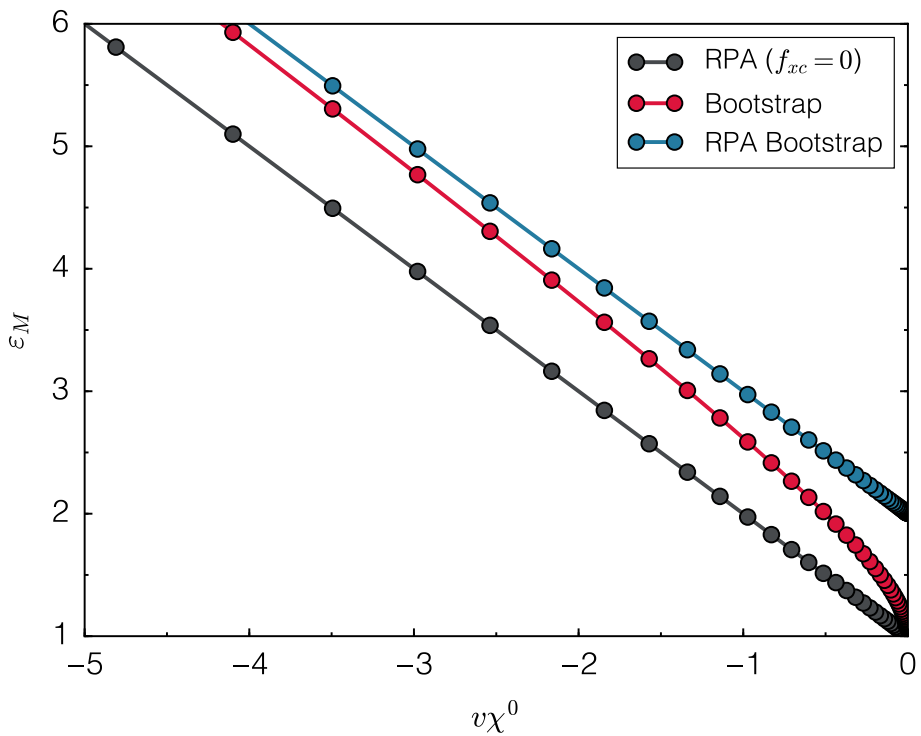
$$f_{xc} = \frac{1}{\epsilon_{\mathrm{M}}^{\mathrm{RPA}} \bar{\chi}^{\mathrm{RPA}}}$$

$$\bar{\chi}^{\mathrm{RPA}} = \chi^0 + \chi^0 \bar{v} \bar{\chi}^{\mathrm{RPA}}, \bar{v}_{\mathbf{G}=0} = 0$$

- Keeping only the $\mathbf{G} = 0$, RPA-BOOTSTRAP is essentially the one-shot version of the original BOOTSTRAP kernel.

- Head-only BOOTSTRAP (no local fields)

$$f_{xc,\mathbf{00}} = \frac{1}{2}\left(\frac{2}{\chi^0_{\mathbf{00}}} - v_{\mathbf{0}}\right) + \frac{1}{2}\sqrt{\left(\frac{2}{\chi^0_{\mathbf{00}}} - v_{\mathbf{0}}\right)^2 - \frac{4}{(\chi^0_{\mathbf{00}})^2}}$$



- $\epsilon_{\mathrm{M}}^{\mathrm{RPA}} = 1 - v\chi^0$
- $\epsilon_{\mathrm{M}}^{\mathrm{RPA\text{-}BOOT}} = 2 - v\chi^0 = 1 + \epsilon_{\mathrm{M}}^{\mathrm{RPA}}$
- $\epsilon_{\mathrm{M}}^{\mathrm{BOOT}}$ inbetween

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Rigamonti: "Once the calculations are settled, the results of the BO are hence disappointing." (Rigamonti et al. 2015)

Sharma: "...these claims are overstated and that these authors were unfortunately misled by focusing on only three materials: Si, Ar, and LiF. ...the RBO kernel significantly worsens the macroscopic dielectric constant." (Sharma, J. K. Dewhurst, et al. 2016)

Rigamonti: "The comment by S. Sharma and coworkers does not contain benchmarks or criticism that are pertinent to our work." (Rigamonti et al. 2016)

Showdown

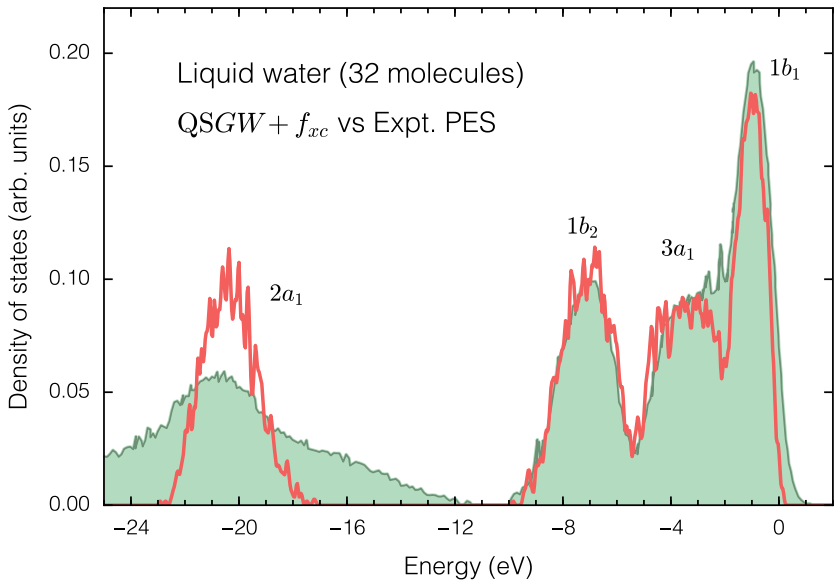
Band gaps obtained with various BOOTSTRAP kernels

	f_{xc}	$f_{xc,0}$	$f^{\mathrm{RPA}}_{xc,0}$	Expt.+ZPR
AlP	2.73	2.82	2.75	2.47
C	5.94	6.00	5.86	5.85
CaS	4.83	5.00	4.80	4.43
CdS	2.66	2.87	2.73	2.48
CoO	2.78	3.47	3.30	2.5
InP	1.55	1.66	1.60	1.47
NiO	3.94	4.53	4.40	4.3
Si	1.30	1.34	1.31	1.22
SiC	2.45	2.48	2.43	2.40
SnO_2	3.55	4.01	3.82	3.6
TiO_2	3.74	3.94	3.84	3.3
ZnSe	2.95	3.25	3.11	2.87

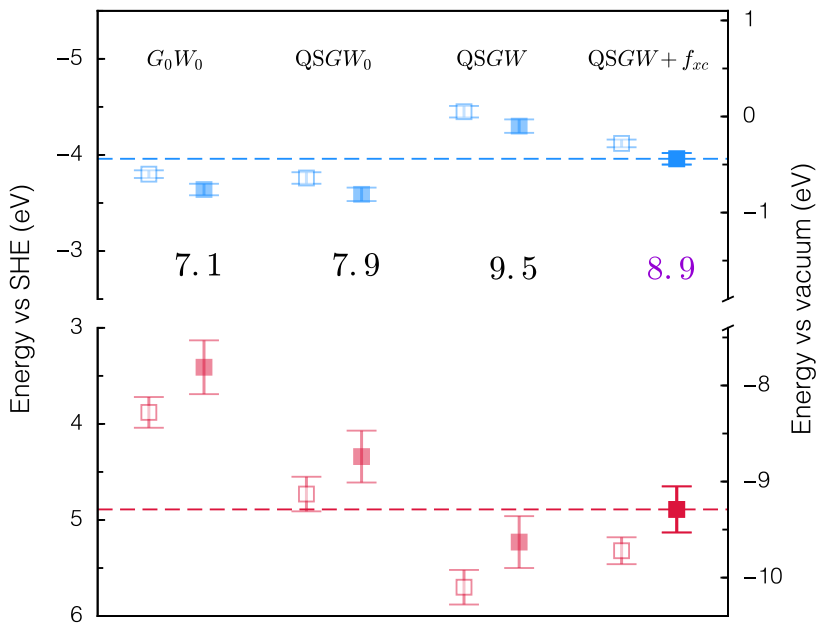
	f_{xc}	$f_{xc,0}$	$f^{\mathrm{RPA}}_{xc,0}$	Expt.+ZPR
Ar	-	14.00	13.29	14.30
BN	6.60	6.72	6.50	6.6
CaO	7.11	7.30	6.94	7.0
LiCl	9.70	9.99	9.57	9.4
LiF	-	14.51	13.76	14.6
MgO	7.88	8.34	7.78	8.12
NaCl	8.84	9.14	8.55	8.5, 8.9
NaF	-	12.17	11.26	11.5
Ne	-	20.11	18.75	21.7

- The original kernel is most consistent.
- Local fields in f_{xc} affect band gaps by 0.1-0.4 eV.
- RPA-BOOTSTRAP strongly underestimates the band gap for "ultra" wide-gap materials.

Applications: Electronic structure of liquid water



"*ab initio* electronic structure of water" (Chen, Ambrosio, et al. 2016)



VBM and CBM of water (filled: w/ nuclear quantum effect).

- E_g = 8.9 eV, vs experimentally determined 8.7 ± 0.6 eV (Bernas, Ferradini, and Jay-Gerin 1997).

Applications: Nonempirical hybrid functionals

- *global*

$$v_x = \alpha \Sigma_x + (1-\alpha) v_x^{\mathrm{KS}}$$

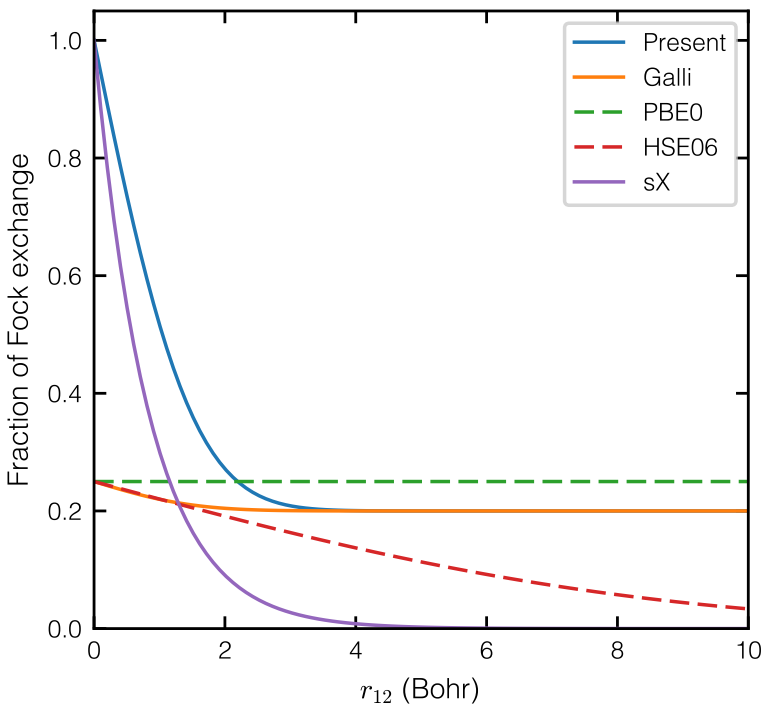
$$\alpha = 1/\epsilon_\infty$$

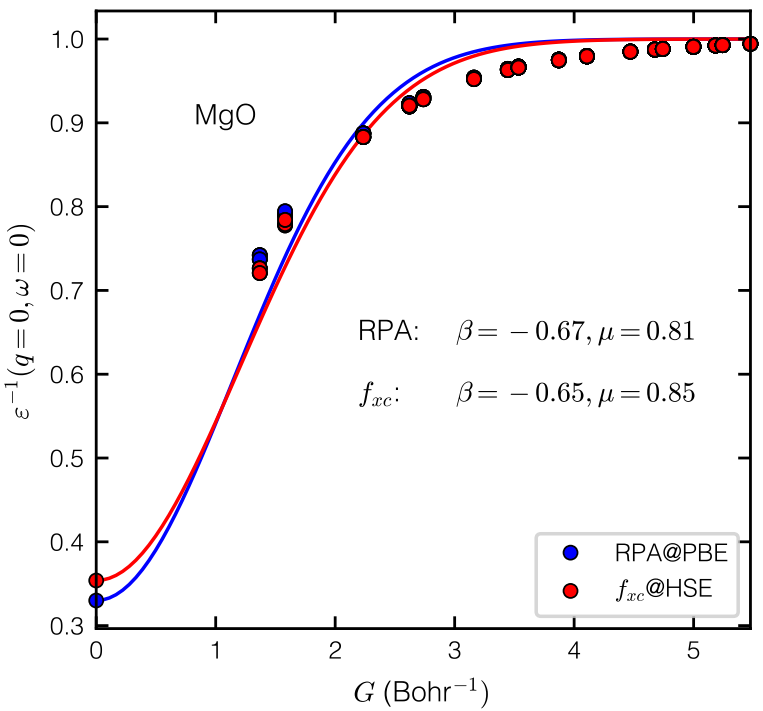
- *range-separated*

$$v_x = \left[\alpha + \beta \mathrm{erf}(\mu r_{12})\right] \Sigma_x - \beta \mathrm{erf}(\mu r_{12}) v_x^{\mathrm{KS}}$$

$$\alpha = 1, \beta = \epsilon_\infty^{-1} - 1$$

$$\varepsilon^{-1} \to 1 + (\epsilon_\infty^{-1} - 1) \exp(-G^2/4\mu)$$





Applications: Nonempirical hybrid functionals

	E_g (eV)		ϵ_∞	
	Hybrid	Expt.	Hybrid	Expt.
AlAs	2.22	2.24	8.13	8.16
AlP	2.52	2.51	7.16	7.54
C	5.61	5.85	5.47	5.70
CdS	2.95	2.48	5.28	5.4
CdSe	1.89	1.84	7.07	6.2
Cu_2O	2.49	2.12	6.36	6.46
GaAs	1.12	1.52	13.98	10.58
GaN	3.50	3.50	5.25	5.30
GaP	2.42	2.35	9.24	9.11
Ge	0.60	0.74	15.38	15.9
InP	1.55	1.42	9.81	9.61
Si	1.14	1.22	11.35	11.9
SiC	2.47	2.40	6.38	6.52
ZnO	3.54	3.4	4.15	3.74
ZnSe	2.68	2.72	6.33	5.9

	E_g (eV)		ϵ_∞	
	Hybrid	Expt.	Hybrid	Expt.
Al_2O_3	9.51	8.8	3.18	3.10
AlN	6.26	6.28	4.18	4.18
Ar	14.67	14.3	1.76	1.66
BN	6.56	6.6	4.39	4.50
CaO	7.17	7.0	3.37	3.33
LiCl	9.89	9.40	2.78	2.70
LiF	15.56	14.60	2.15	1.90
MgO	8.19	8.12	3.08	2.96
NaCl	9.10	8.9	2.38	2.40
Ne	22.51	21.7	1.41	1.23

(WIP)

Conclusions

- QSGW with BOOTSTRAP vertex corrections is reliable for band-gap predictions.
- NANOQUANTA accuracy achieved at (nearly) no overhead w.r.t. RPA.
- "Ultra" wide band-gap insulator are still a challenge for BOOTSTRAP.
- Available in ABINIT v8.0+ (`gwgamma`).

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